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UNITED STATES DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
WASHINGTON, D. C.

Letter
Circular
LC-444

(July 13, 1935)

(Revision of Letter Circular 61 issued April 26, 1922, and revised March 19, 1927)

HARDENED COPPER

To meet the frequent requests for information on the subject of "Hardened Copper" this letter circular has been prepared.

The so-called "lost art" of hardening copper is no secret from present day metallurgists, and no reward for its discovery has been offered by the Government. Rumors to that effect have been circulated and the Bureau has received many inquiries concerning it, such requests for information being usually prompted by newspaper stories such as that of the rediscovery of the art by an automobile mechanic and its subsequent sale for a fabulous sum.

There is nothing new or "mysterious" in "hardened copper"; immense quantities are in commercial use and more is being added daily. Any well-informed metallurgist today knows how to produce an edged tool of hardened copper as good as any made in prehistoric times, but the knowledge does him no good because of the superiority of the steel tools now available. This result, which has been the goal of many an amateur inventor, can be attained by any one of three well-known processes, or by a combination of them. Briefly, the three hardening processes depend upon (a) cold working, (b) alloying and (c) heat treatment (after alloying).

Hardening (or "tempering") may be produced by cold rolling or hammering, cold-drawing, etc. Hard drawn copper wire and cold drawn tubing are examples. To supply the needs of a single industry alone, vast quantities of copper hardened by this means are used in hard drawn trolley wire.

The second method of hardening copper is to alloy it with a small amount of another metal or perhaps more than one metal. Zinc, tin, aluminum, and iron are the common additions. The alloyed metal, of course, should not be

referred to as "copper", but should be named according to the chief alloying constituent, i.e., brass, bronze, etc. This name may be further restricted according to other additions, e.g., zinc-bronze, nickel-brass, etc. Vast quantities of copper hardened in this general way are in commercial use. Many of the samples of "hardened copper" submitted to this Bureau for examination have been found to contain small amounts of one or more of the elements named above.

One of the favorite methods of "hardening" copper appears to consist in manipulating the melting (perhaps unwittingly on the part of the experimenter) so that the resulting melt is impregnated with oxide. Cuprous oxide is soluble in molten copper and alloys with it in exactly the same sense that a metal does. Copper hardened in this way is considerably harder and more brittle than the pure metal, but is unsuited for most of the purposes for which copper is used.

The term "hardened copper" has been used above in its general sense to refer to copper in which the mechanical properties have been modified in the manner usually understood by the term "hardening", i.e., an increase in toughness, a decrease in ductility, etc. The popular conception of "hardened copper", however, is that of a metal similar to hardened steel and usually implies the "ability to carry a cutting edge".

Of the numerous samples of "hardened copper" submitted to this Bureau for examination, many were found to be impregnated with cuprous oxide, which indicates that alloying with oxide had occurred during the melting as described above. Such a product is considerably harder and more brittle than pure copper and has a characteristic red color. Samples of "hardened copper" submitted by one inventor were analyzed by the Bureau and found to be simply aluminum bronze, an alloy well known for many years and having considerable industrial use at present. The attempt had also been made to "stiffen" the material by rolling. Several years ago a manufacturer of aluminum bronze distributed a small cold chisel of this material as an advertising novelty. This chisel would actually cut soft steel, though its edge was soon dulled. It was superior to the bronze and "hardened copper" axes of prehistoric times, however, and in those days would have constituted a metallurgical advance. To the modern metallurgist, it is only an interesting toy.

The following determinations of the Brinell hardness of different forms of copper and of a sample of so-called "hardened copper" submitted to the Bureau are of some significance:-

Specimen	Bhn (500 kg load, 10 mm ball)
Hard-drawn trolley wire (23/64" diameter)	107
Hot-rolled; 1/4" sheet	68
Electrolytic (cathode) copper as deposited	59
"Hardened" copper, as submitted (sample contained 5.5 per cent zinc)	39

Popular interest in the so-called "lost art" of hardening or "tempering" copper is evidenced by the rather numerous patents covering such processes. The directions given in some of these patents for the treatment of the metal are very suggestive of the methods of working metals used in medieval times. The following may be quoted as typical:

> "Heat the copper to 260° to 315° and subject it while hot to fumes of burnt sugar and animal fat at a temperature below that necessary to form carbon monoxide."

No industrial application appears to have been made of these patented methods for "hardening" copper.

In fact, in the industrial use of copper itself, it is often desired to increase the ductility rather than to increase the hardness. Webster, Christie, and Pratt (Some comparative properties of tough-pitch and phosphorized copper, Proc. Inst. of Metals, Am. Inst. Mining and Metallurgical Engineers, 233, 1927) have shown that, by reducing the oxygen content of copper through a deoxidation process which leaves about 1/100 of 1 percent of phosphorus in the metal but nevertheless raises the copper content, i.e., the purity, from, say, about 99.935 percent to about 99.97 percent, the strength is not altered, but the ductility and workability are increased.

The search for new and better alloys of copper which may combine strength and resistance to corrosion, or strength and good electrical conductivity, is being unremittingly carried on by scientists. In ancient times weapons and cutting tools were sought; today the needs which the non-ferrous metallurgist seek to fill are, rather, those for better materials to resist

corrosion, as in the manufacture of chemicals or the carrying out of chemical processes; for strong, cheap and weather-resistant roofing materials; and for better cables, trolley wires, and other electrical conductors.

Some of the copper alloys being studied by scientists with the idea of finding alloys suitable for these modern purposes are decidedly harder than pure copper. Corson has demonstrated (Copper hardened by new method, Iron Age, 119, 424 (1927), also Bain, Notes on the atomic behavior of hardenable copper alloys, Proc. Inst. Metals, Am. Inst. Mining and Metallurgical Engineers, 451 (1927).) that various alloys of copper, silicon and a third metal such as nickel, chromium, or cobalt, in which the third metal forms a silicide, nickel silicide, for example, may be made strong and hard by heat treatment. Such a treatment consists in heating to such a temperature that the silicide goes into solid solution in the copper, quenching to retain the silicide in solution, (after which the alloy is still soft) and then reheating or tempering to secure a controlled precipitation of the silicide. The precipitation of the fine particles of silicide hardens the alloy in a manner similar to the hardening of the heat-treatable aluminum alloy, duralumin. This is the third method of hardening. But since there are needed several percent of alloying elements to secure a marked ability to be hardened by quenching and tempering, such alloys are classed as alloys, not as "hardened copper" or "hardened aluminum".

The most important development along this line is copper containing a small percentage of beryllium. Beryllium forms alloys with copper in all proportions but the commercially useful alloys are limited, at the present time, to those containing from about 0.7 to 2.5 percent of beryllium. In this range of beryllium content, the copper alloys (beryllium bronzes) are hardenable by the duralumin type of hardening treatment. The alloys are ductile and soft when quenched in water from about 800°C and become hard when heated subsequently to about 350°C. Tensile strengths approaching 200,000 lb per square inch and Brinell hardness numbers as high as 400 can be obtained. The physical properties of the beryllium-copper alloys have been investigated in detail and they are such that many useful applications can be made of the alloys. The cast alloys are hardenable as well as the wrought alloys but require somewhat longer hardening treatment and do

not develop quite as high tensile strengths. A very promising use is for "non-sparking" tools, hammers, chisels, etc. Another use is as a spring material especially for elevated-temperature service.

While newspaper headlines referring to these newer alloys of copper may refer to them as "hardened copper" and to imply that ancient secrets are being rediscovered, the metallurgists who have developed these alloys would be the last to make such statements or to perpetuate the erroneous idea that these alloys can compete with modern tool steels for edged tools.

Relative to the so-called "lost art of hardening and tempering copper or bronze", the following quotation from Wm. Gowland (J. Inst. Metals, VII, 23 (1912) is of interest. Professor Gowland formerly of the Royal School of Mines, London, was an authority upon the metallurgy of copper and its uses in antiquity.

> "The castings (knives, swords, etc.) generally were hammered at their cutting edges, and it is to this hammering and to it only, that the (increased) hardness of the cutting edges of both copper and bronze weapons is due, and not to any method of tempering. Much has been written about the so-called art of tempering bronze, supposed to have been practiced by the men of the Bronze Age in the manufacture of their weapons; the hardness is also said to be greater than can be given to bronze of the present day. I should like to correct this error, as it can only have arisen owing to its authors never having made any comparative practical tests of the hardness of bronze. Had they done so, they would have found that the ordinary bronze of today can be made as hard as any, in fact harder than most, of prehistoric times, by simple hammering alone."

It is, of course, not impossible that some of the ancient bronze implements may have owed part of their usefulness as weapons to the presence of certain impurities which served to harden the alloy and give it a fair cutting edge when heat treated in some fashion. Nickel is found in many of the ancient bronzes (Gowland, J. Inst. Metals, 7, 23 (1912); Chickashige, Trans. Chem. Soc., 117, 917 (1920), and silicon, though seldom reported in analysis of ancient copper alloys, might have been present in some. It appears

most probable, however, that the hardening effect of tin which was often present, was the chief source of the hardness of the weapons and it is unlikely that hardness was obtained by quenching and tempering.

The following articles on the subject of "hardened copper" taken from recent literature may be consulted. They show an agreement in opinion as to the merits of "hardened copper" with that of this Bureau stated above. These articles are available in most of the larger technical libraries, or may be purchased in photostat form from the Engineering Societies Library, 29 West 39th Street, New York City for a nominal fee.

"Tempered copper phantasies", A. Bregman, Metal Industry, 23, 279 (July, 1926).

"Open season for hardened copper", Chem. and Metal. Eng., Number 32, 751 (October, 1925).

"The lost arts", W. E. Henderson, Ind. and Eng. Chem., News Edition, September 20, 1925, p. 12.

"The hardened copper myth", E. C. Gleason, Metal Industry, Number 22, 352 (September, 1924).

"Hardened copper", Chem. and Metal. Eng., Number 31, 215 (1924).